

MAPPING PHASE DIAGRAMS OF CARBONATES AND ESTERS: EXPLORING LOW-TEMPERATURE FRONTIERS FOR THE OPERATION OF BATTERIES AND CAPACITORS

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1. INTRODUCTION

Reliable operation at low temperatures for batteries and capacitors is a key requirement for military applications. These applications often entail usage of the devices in extreme conditions; operating temperatures as low as $-60\text{ }^{\circ}\text{C}$ have recently made their appearance in the requirement for some lithium-ion batteries. It is therefore incumbent upon us to survey the landscapes and explore the frontiers of low-temperature operation for the battery and capacitor devices, frontiers delineated by the physical properties and processes of the device materials and thus delineating the periphery for the successful formulation of these low-temperature devices.

Among the factors delineating the frontiers, the most inflexible and punishing is the freezing of the liquid electrolytes. It is inflexible because the freezing point of an electrolyte is unalterable once it is formulated and placed in a device and the onset of the freezing can hardly be circumvented by such means as fast cooling or short stay at a low temperature. It is punishing because the liquid electrolyte of a battery or capacitor is the medium through which the ions—the carriers of the energy to be stored and released—have to swim between the two electrodes for the acts of the storage and release; therefore, a frozen electrolyte means a dead device.

The freezing of an electrolyte is predominantly determined by the freezing of the solvent, which forms the electrolyte by dissolving a salt in it. The freezing, or precipitation, of the salt is not a consideration because practical batteries and capacitors contain only a small amount of salt in their electrolytes. The freezing point of a solvent, on the other hand, can vary a great deal, depending on its nature and composition. The freezing point of a pure solvent is the same as its melting point and is thus fixed. But this melting point can be significantly lowered with the addition of a second solvent component, which in turn can be further lowered with the addition of a third, and so on. Mapping out the freezing points at various solvent compositions, through measurement and computation, for the most useful solvents for non-aqueous batteries and capacitors, is the goal of this work. These useful solvents are mixtures of organic carbonates and esters, which possess exceptional chemical stabilities and other favorable properties.

2. MEASUREMENTS, CALCULATION, AND RESULTS

The mapping of the phase diagrams began with the measurement for solvent mixtures of two components—the binary phase diagrams, by measuring the phase transition temperatures of different binary solvent mixtures.^{1,2} These temperatures included the liquidus and solidus temperatures determined with a differential scanning calorimeter by heating through the associated phase transitions at the rate of 2 K/min a sample mixture that had been crystallized by cooling it well below its eutectic point. When these measured liquidus and solidus temperatures were plotted as functions of solvent composition, a binary phase diagram resulted.

These experimental phase diagrams enabled the binary interaction parameters between the different solvent components to be evaluated, by fitting to them thermodynamic models that contained these parameters. These models are all non-ideal solution models in which the Gibbs free energy of mixing between components A and B is expressed as

$$\Delta_{\text{mix}}G = \sum_i x_i \Delta_{\text{fus}}G_i + RT \sum_i x_i \ln x_i + x_A x_B L_{AB} \quad (1)$$

where x is the mole fraction, T temperature, R the gas constant, and i runs through A and B. The Gibbs free energy of fusion

$$\Delta_{\text{fus}}G_i = \Delta_{\text{fus}}H_i \left(1 - T/T_{m,i}\right) + \int_{T_{m,i}}^T (C_{p,i}^l - C_{p,i}^s) dT - T \int_{T_{m,i}}^T (C_{p,i}^l - C_{p,i}^s) dT \ln T \quad (2)$$

where $\Delta_{\text{fus}}H_i$ is the enthalpy of fusion at the melting point $T_{m,i}$, and $C_{p,i}^l$ and $C_{p,i}^s$ are the heat capacities in the liquid and solid states at T for the component i . The binary interaction parameter, L_{AB} , is set to a quadratic polynomial function of solvent composition x_i :

$$L_{AB} = a_0 + a_1 x_i + a_2 x_i^2 \quad (3)$$

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Once the coefficients of Eq. 3 are specified in value, Eqs. 1-3 would yield, through computation, a set of numerical values that delineate the solid-liquid phase diagram for the A-B binary, i.e.,

$$x = f(T, a_0, a_1, a_2) \quad (4)$$

Conversely, by fitting Eq. 4 with a set of undetermined parameters a_0 , a_1 , and a_2 to the measured phase diagram, these parameters can be evaluated and the L_{AB} of Eq. 3 can thereby be determined. This fitting was achieved by minimizing the target function

$$S(a_0, a_1, a_2) = \left(\sum_i^A + \sum_i^B \right) [f(T_i, a_0, a_1, a_2) - x_i]^2 + n(f^A - f^B)^2 (T_{eu}, a_0, a_1, a_2) \quad (5)$$

where T_{eu} is the eutectic temperature of A-B, A and B denote the solubility curves of A in B and B in A, respectively, and n the number of times the eutectic point has been measured at different compositions.^{3,4}

Finally, the ternary and quaternary phase diagrams were calculated with the equation

$$\Delta_{\text{mix}} G = \sum_i x_i \Delta_{\text{fus}} G_i + RT \sum_i x_i \ln x_i + \sum_i \sum_{j>i} x_i x_j L_{ij} \quad (6)$$

where i and j run through all the components of the solvent and the ternary and quaternary interaction parameters were all assumed to be zero. A ternary example of the results is shown in Fig. 1, which demonstrates a liquidus surface expanding downwardly from the melting points of the three components making a eutectic point as low as about -100°C .⁵ An electrolyte of practical concentration with this eutectic solvent would have a melting point well below -100°C .

3. CONCLUSIONS

Binary phase diagrams of carbonates and esters were systematically measured, and the binary interaction parameters were thereby thermodynamically and computationally evaluated. Based on these parameters, ternary and quaternary phase diagrams were reliably calculated and plotted for the carbonates and esters. The results showed that the freezing point of a solvent can be effectively lowered by adding the right solvent component in the right amount and electrolytes as low-melting as -100°C can thus be formulated. The effectiveness could be further enhanced by adding a component with properties similar to the host component whose freezing dominates that of the electrolyte.

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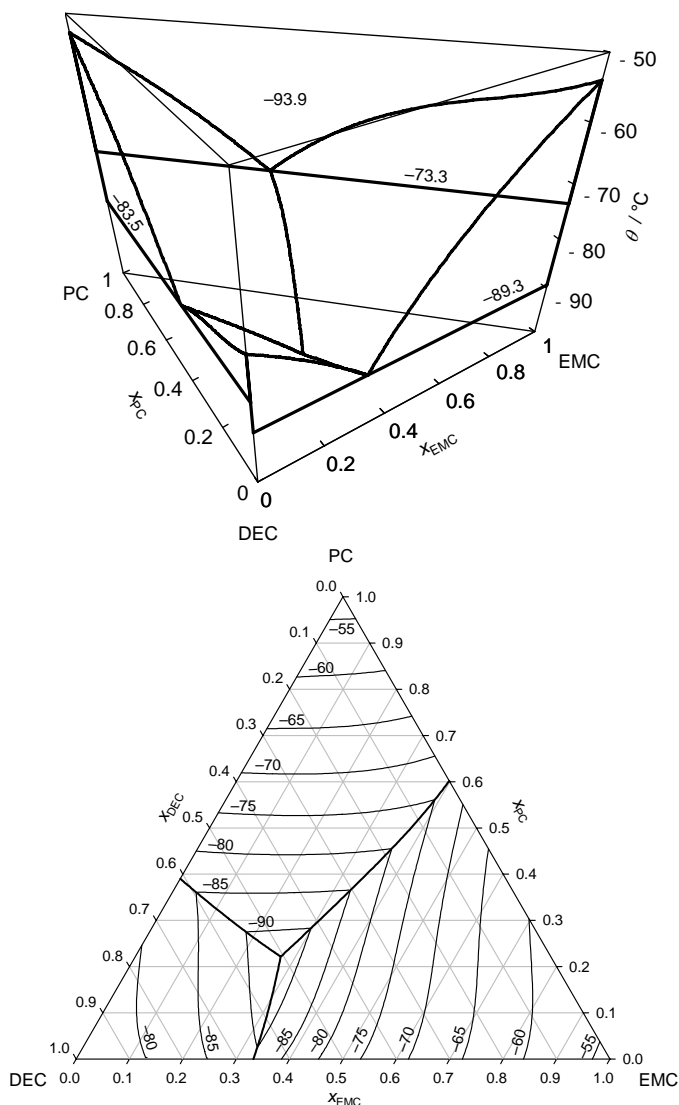


Figure 1. Liquidus surface of EMC + PC + DEC ternary carbonate as a surface plot (upper) and a contour plot (lower) of temperature θ over the composition triangle of mole fraction x .